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Perfluoropolyalkylether Oil Degradation: Inference of FeF₃ Formation on Steel Surfaces under Boundary Conditions

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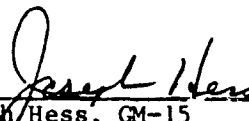Los Angeles, CA 90009-2960

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The formation of iron fluoride (FeF_3) through the interaction of Kaytox 143AB perfluoropolyalkylether (PFPE) oil with steel surfaces was investigated under boundary lubrication conditions. Ball-bearing rolling action was simulated by a specially designed wear-test apparatus that incorporated noncoaxial wear members to give a skid/roll ratio of ~0.16. The contact stress was 8.3×10^8 N m^{-2} (~120,000 psi), and the speed was 1750 rpm. Under these conditions, FeF_3 formation on the wear surfaces was inferred

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using X-ray photoelectron spectroscopic (XPS), Auger electron spectroscopic (AES), and secondary ion mass spectrometric (SIMS) surface analysis techniques. These findings support the hypothesis that, under the low oxygen environment of spacecraft earth orbit, formation of FeF_3 and subsequent FeF_3 catalyzed degradation of PFPE can constitute an important PFPE degradation pathway under boundary lubrication conditions.

PREFACE

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with the wear-test apparatus, and J. L. Childs, N. Marquez, S. A. Jackson,
and R. Bauer for the XPS, IMMA, AES, and profilometry analyses, respectively.

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I. INTRODUCTION

Because of the increasing use of perfluoropolyalkylether (PFPE) oils (Scheme I) in spacecraft systems, it is important to understand the degradation mechanisms so that the usefulness of these lubricants will not be extended beyond their capabilities. In a previous report, we hypothesized a two-step mechanism that contributes to the degradation of PFPE oils used as lubricants in ball bearings: 1) interaction between PFPE and the iron in the steel to form the Lewis acid FeF_3, followed by 2) catalytic cleavage of PFPE by FeF_3 to form lower molecular weight reactive products.[1] In the absence of oxygen, such as in the spacecraft orbital environment, this mechanism may well be the dominant degradation pathway.

$$R_f \left(\begin{array}{c} CF - CF_2 - 0 \\ | \\ CF_3 \end{array} \right)_n R_{f'}$$
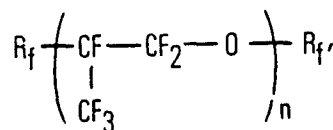
Scheme I

R_f and R_f' = perfluoropolyalkylether end groups of unspecified length; $n \sim 20$.

The second step, the reaction of PFPE with FeF_3, has been reported to be significant at temperatures that are $\sim 30°C$ below the onset of thermal degradation.[1] Although the reaction temperatures are high, they are consistent with the lower estimates of ball-bearing asperity contact temperatures.[2]

The interaction of PFPE with iron (mechanistic step 1) has not received much attention in the literature. Several research groups have inferred the formation of metal fluoride salts in the reaction of PFPE oils with aluminum and ferrous alloys under oxygen-containing atmospheres[3] and with titanium under oxygen and nitrogen.[4] The interaction of fluorocarbon compounds with iron metal (oxidized iron would be unreactive) leading to dehalogenation has been observed in systems in which aromatic reaction products are formed from

nonaromatic reactants but has not been reported for systems in which aliphatic products are formed.[5] The aromaticity undoubtedly influences the reaction energetics by stabilizing both the transition state and products. The identity of the iron-containing products in these reactions was not reported.

Reported here is one aspecc of the PFPE oil degradation mechanism: the formation of FeF_3 through the interaction of PFPE with iron.

II. EXPERIMENTAL

A. MATERIALS

The PFPE oil used in these experiments was a commercially available product (Kaytox 143AB) with the nominal structure given in Scheme I. Table 1 lists the oil's properties. PFPE with ~2 weight percent hydrocarbon oil contaminant was also investigated in conjunction with another research program. FeF_2 and FeF_3 were reagent grade and were used without further purification.

B. WEAR-TEST FIXTURE

The wear-test fixture used for the tests is depicted in Fig. 1. It was designed to achieve boundary conditions tr·ough a combination of ball skidding and rolling action at contact pressures typical of ball-bearing applications. The design philosophy was to stress the lubricant so that degradation and failure would occur in a reasonable test time and to provide samples for surface analysis.

The primary wear interaction occurs between a flat, 32 mm diameter, 440C stainless-steel disk that is rotated by a 37.3 W dc motor and an F1 thrust bearing. The nominal rotational speed was 1750 rpm, although several tests at 4000 rpm were run at the beginning of the program. The balls (4.76 mm diameter, 440C) are held between the disk and the normal thrust bearing raceway. The F1 bearings contained ten balls. The raceway is attached to the bottom of the fixture housing. The unique feature of the fixture is that the rotational axes of the disk and the thrust bearing are not coaxial, but are eccentric by ~1 mm. This eccentricity results in a skid/roll ratio of ~0.16 and a wear track on the disk that is about 2.5 to 3.0 mm wide. The average diameter of the wear track is ~22 mm. The disk is centered by a guide thrust bearing that is loaded axially by a calibrated spring. Compression of the spring when the apparatus is assembled results in a load of 44.5 N on the disk-bearing pair. This is equivalent to a calculated Hertzian contact stress of 8.3×10^8 $N \cdot m^{-2}$ (~120,000 psi) at the ball-disk interface. A high-vacuum

TABLE 1. PFPE OIL PROPERTIES

Viscosity at:	
37.8°C	$85 \text{ mm}^2 \cdot \text{s}^{-1}$
98.9°C	$10.3 \text{ mm}^2 \cdot \text{s}^{-1}$
Viscosity index	113
Pour point	-43°C
Density at 23.9°C	$1.89 \times 10^3 \text{ kg} \cdot \text{m}^{-3}$
Surface tension at 26°C	$1.85 \times 10^{-2} \text{ N} \cdot \text{m}^{-1}$
Vapor pressure at:	
149°C	40.1 Pa
204°C	334 Pa
260°C	1377 Pa
315°C	7019 Pa

GUIDE BEARING
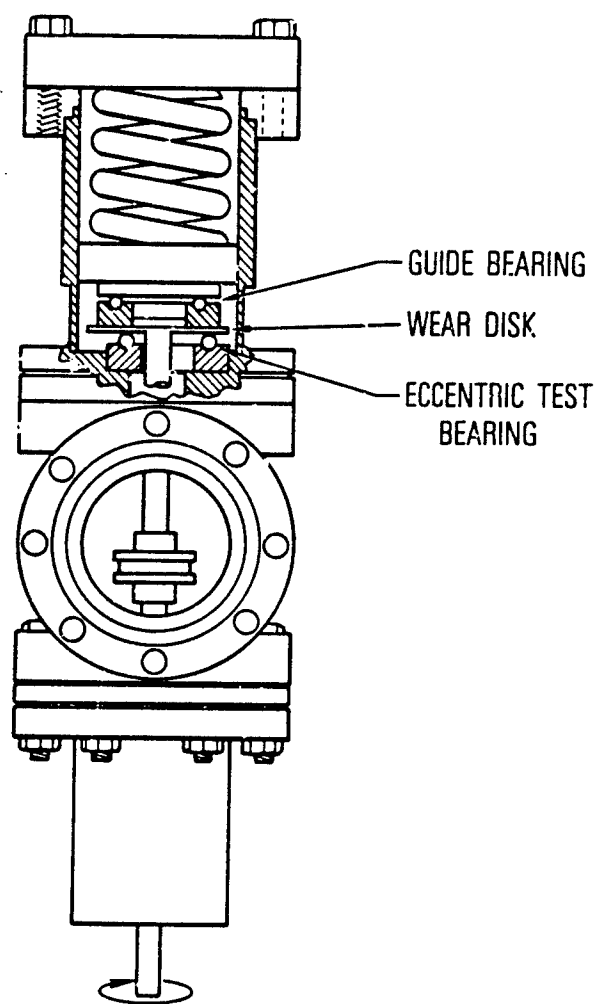
WEAR DISK

ECCENTRIC TEST BEARING

Fig. 1.   Wear-test fixture.

feedthrough connects the disk to the motor. The entire apparatus is housed in stainless-steel vacuum components and is connected to a liquid nitrogen trap to capture potentially hazardous PFPE volatile degradation products. The trap is connected to a turbomolecular vacuum pump. The pressure in the apparatus was not measured but can be estimated as follows: The turbomolecular pump will not operate at maximum turbine speed unless the pressure is $\lesssim 1.3 \times 10^{-1}$ Pa. In all the tests, the pump achieved full turbine speed in a short time, suggesting that the equilibrium pressure was considerably less than this value. The lowest pressure is limited to $\gtrsim 1.3 \times 10^{-5}$ Pa by the use of polymeric flange seals. Thus, the estimated test pressure, P, is 1.3×10^{-5} Pa $\lesssim P \lesssim 1.3 \times 10^{-1}$ Pa.

The tests were run at the ambient laboratory temperature, and no attempt was made to control or measure the temperature of the fixture. The system torque was originally intended to be used as a measure of the degradation in the system; a large torque increase would indicate that the test should be terminated. The torque was measured indirectly by monitoring the voltage drop across a precision 1 ohm resistor in series with the motor. Although the system sometimes exhibited obvious degradation, the torque did not show consistent increases but instead displayed inconsistent changes in noise. As a result, the torque was not an adequate indicator of the state of the system. Instead, 48 h was arbitrarily selected as test duration, and the wear surfaces were examined to determine relative lubricant performance and wear. The test conditions are given in Table 2.

C. WEAR-DISK ANALYSES

Following each test, the apparatus was disassembled and the disk, balls, and thrust bearing raceway were rinsed with 1,1,2-trichloro-1,2,2-trifluoro-ethane (Freon TF) solvent to remove remaining lubricant. (The rinses were analyzed by chromatographic and spectroscopic techniques; however, there was insufficient residual lubricant to give meaningful results.) The wear disks were cut in half with a carbide saw so there would be pieces small enough to fit the sample carousel of the XPS spectrometer. Polymerized fluorocarbon lubricant was removed by heating the disk samples in a bell jar vacuum system

TABLE 2. PFPE WEAR-TEST CONDITIONS

Speed	4000 rpm[a]
	1750 rpm[b]
Axial load	44.5 N
Hertzian contact stress	$\sim 8.3 \times 10^8$ N·m^{-2}
Pressure	$\sim 1.34 \times 10^{-5}$ Pa
Test duration	2-4 h[a]
	48 h[b]

[a]Initial tests; failed too quickly

[b]Nominal test conditions.

to between 390 and 420°C at a pressure of ~1.34×10^{-4} Pa for 48 h, which resulted in pyrolytic decomposition of the residual polymeric material. The disk samples were analyzed by X-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS), Auger electron spectroscopy (AES), and profilometry to determine wear at the disk surface and lubricant degradation. Samples of FeF_3 and FeF_2 were examined by XPS and SIMS techniques.

In XPS, the chemical shift of the signal for an element is a function of the originating atom's identity and valence state. Thus, it is possible to differentiate between signals caused by fluoride ion (685 eV) and covalently bonded fluorine (689 eV) as found in fluorocarbons. (The spectra were referenced to adventitious carbon at 285.0 eV.) In addition, the intensity of the XPS signal is approximately proportional to the element surface concentration. In the SIMS technique, a focused beam of energetic ions (in this case, O_2^+) sputters away the surface of the sample generating, among other particles, ions that can be analyzed by mass spectrometry. The ion molecular weight distribution gives information about the surface composition of the sample. Our intention was to search for ions corresponding to FeF_3 on the disk surface. In AES, identification of surface elements is achieved. With the rastering capability of the instrument, elemental maps can be used to ascertain the surface spatial distribution of specific elements.

III. RESULTS AND DISCUSSION

A. XPS AND PROFILOMETRY ANALYSES

Figure 2 shows the XPS spectrum in the fluorine chemical shift region of the wear-disk surface from wear-test number 4, in which pure PFPE was used. Because the X-ray excitation and analysis window and the wear track are approximately the same size, the signals come primarily from the wear-track area, as desired. The signal observed on the wear-disk wear-track area is for fluoride ion at 685 eV (curve A). An XPS spectrum of fluorocarbon oil covalently bonded fluorine (curve B) is included for comparison. (The small emission at 681 eV in curve B is an X-ray satellite due to an additional line in the X-ray source.) The XPS iron peaks were not included in these analyses because the peaks are weak and the diversity of iron compounds, i.e., oxides, fluorides, and metal, leads to complicated XPS spectra that are not useful.

There was concern that heating the samples might cause the residual fluorocarbon material to react with the iron, producing fluoride ion. This is unlikely because 1) an unused sample disk covered with PFPE fluid was heated in the bell jar along with the other wear-test samples and exhibited no fluorine or fluoride ion when analyzed by XPS. Reaction of PFPE with exposed, unoxidized metal during disk heating is not likely because of oxygen diffusion and subsequent metal oxidation prior to heating. A simple, conservative permeability calculation using an oxygen permeability constant for fluorinated ethylene-propylene (FEP) fluorocarbon polymer[5] indicates that during 24 h storage at ambient conditions, $>1 \times 10^4$ times as much oxygen as is necessary to provide monolayer coverage can diffuse through the residual fluorocarbon and interact with any unoxidized iron at the substrate-residue interface. Since the wear disks were stored for periods >24 h, it is highly unlikely that reactive iron metal would be present at the interface at the onset of sample disk heating. 2) The reaction of iron metal with perfluorocyclohexane derivatives requires a temperature of 500°C to be significant, and the reaction is aided by incipient aromaticity in the perfluoroaryl products.[6] Although temperatures in excess of 500°C would be expected for dehalogenation
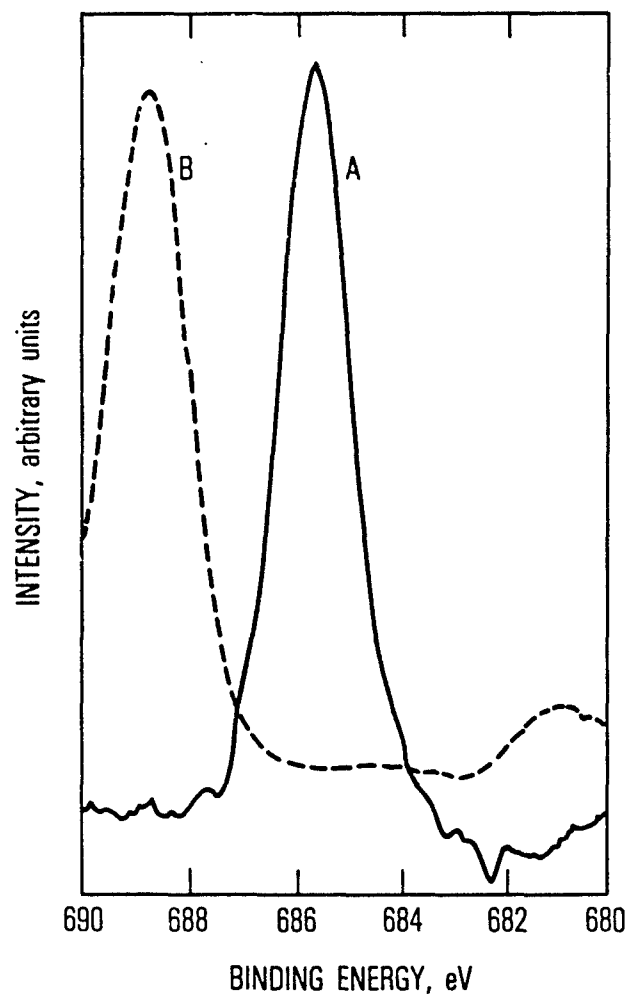
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Fig. 2. Fluorine XPS spectra: A--wear-disk fluoride ion spectrum; B--fluorocarbon fluorine spectrum.

of PFPE and polymerized PFPE by iron, 500°C can be considered to be a lower limit. The pyrolysis temperature in our experiments never exceeded 420°C.

In response to a specific program application, we analyzed the wear behavior of PFPE with and without a 2 weight percent hydrocarbon oil contaminant. Seven samples, three of which used the contaminated oil, were run on the wear-test facility under the conditions given in Table 2. The results of these runs are given in Table 3. After 48 h of testing, the contaminated PFPE lubricated samples obviously outperformed those using pure PFPE. The surface roughness and fluoride ion signals are significantly larger for the uncontaminated samples. From the Table 3 data, one can conclude that the contact temperatures were sufficient to cause iron-fluorocarbon reactions to occur even for the contaminated PFPE samples, despite the fact that very little wear is apparent in the contact areas on the disks.

B. AES ANALYSIS

A fluorine elemental map at the edge of the wear-disk wear-track area for sample number 4 is shown in Fig. 3. The higher intensity observed in the wear-track area is indicative of significantly higher fluorine concentrations than observed outside the wear track.

C. SIMS ANALYSIS

SIMS analysis was performed on one of the wear-disk samples from the early 4000-rpm tests. In addition to stainless-steel constituents and background signals in the wear track, strong signals at $m/e = 75$ and 19, corresponding to FeF^+ and F^+, respectively, were observed, indicating that iron-fluorine compounds were present. There was no indication of FeF_2^+ or FeF_3^+ ions in the spectrum. Outside the wear track, the F^+ and FeF^+ signals were very small, indicating that fluorine-containing compounds were formed in the wear track during wear and did not result from decomposition and reaction of residual fluorocarbon material during heating of the sample disks. SIMS spectra of FeF_2 and FeF_3 powders that were pressed onto indium for analysis exhibited peaks for F^+, FeF^+, and Fe_2^+. Consistent with the observations in the wear track, there was no evidence of FeF_2^+ and FeF_3^+ ions. Apparently, the FeF^+ ion is very stable and FeF_3 and FeF_2 split off F_2 and F atoms

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TABLE 3.   XPS AND PROFILOMETRY ANALYSIS OF WEAR-TEST SAMPLES[a]

TEST NUMBER	LUBRICANT	F^- PHOTOELECTRON COUNTS[b]	SURFACE ROUGHNESS[c]
1	PFPE	19,000	10
2	PFPE	13,000	3.5
3	PFPE	9,500	1.5
4	PFPE	35,000	2.5-3.0
5	PFPE + HC[d]	5,000	0.2-0.5
6	PFPE + HC[d]	7,700	1.0-1.8
7	PFPE + HC[d]	9,500	0.2-0.5
8	Unused disk[e]	-	0.2-0.3

[a]The wear-test conditions were 1750 rpm for 48 h.

[b]Photoelectron counts are proportional to surface concentration.

[c]Size of largest surface features in wear track, in micrometers.

[d]2 weight percent hydrocarbon oil contaminant.

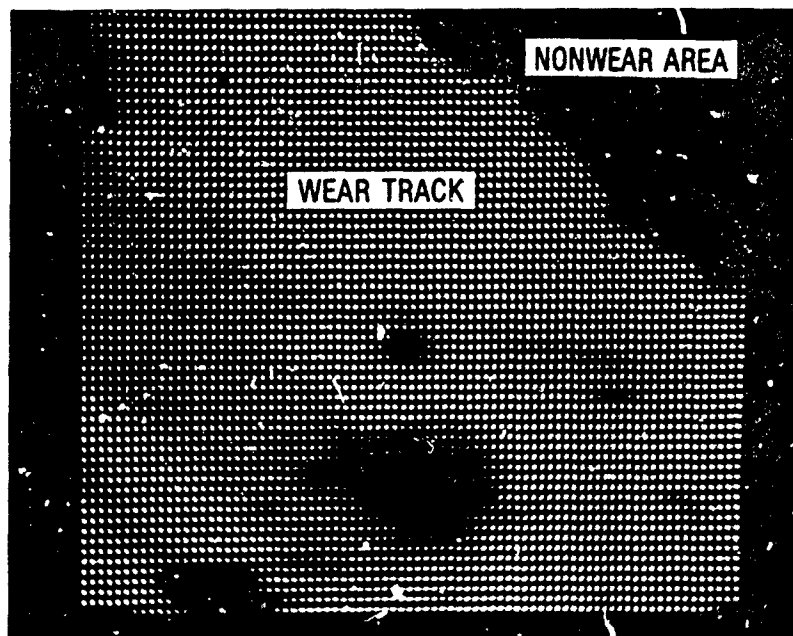[e]All unused disks exhibited surface roughness in this range.

Fig. 3. AES fluorine elemental map at edge of wear track; wear test number 4, 150×.

preferentially to give this ion. These data are compelling evidence for the formation of FeF_x compounds in the wear track.

The issue that needs to be addressed is, Is it FeF_3 that is formed? FeF_2 is not a strong Lewis acid and would not be catalytically active in these reactions. Although the results are not conclusive, the preference for FeF_3 formation can be rationalized on the basis of the oxidizing capability of fluorine. The presence of fluoride ion as well as oxidized iron is consistent with oxidation-reduction reactions taking place. The oxidation potential of fluorine is sufficient to readily oxidize Fe^0 and Fe^{+2} to Fe^{+3}.[7] The presence of fluoride ion implies that the iron is most likely in the +3 oxidation state.

D. MECHANISTIC IMPLICATIONS

The presence of iron fluoride in the wear track can be inferred and is consistent with the mechanistic hypothesis for PFPE degradation under boundary lubrication conditions. The degradation of the oil is initiated by high temperature interaction between PFPE and freshly formed metal surfaces in the contact area generating FeF_3 in catalytic amounts. The FeF_3 catalyzes the scission of the PFPE carbon-oxygen bonds at much lower temperatures than those required for thermal decomposition, resulting in reactive degradation products and polymeric fluorocarbon compounds that react with the iron and further degrade the metal surfaces. The mechanism is autocatalytic.

The inferred presence of iron fluoride also allows a minimum contact temperature of 500°C to be estimated for our system because temperatures of this magnitude are required for the iron-PFPE reaction to be significant.

IV. CONCLUSIONS

The experimental results lead to the following conclusions:

1. From the experimental data, FeF_3 formation on bearing surfaces through the interaction of PFPE with iron under boundary lubrication conditions can be inferred.

2. In the absence of oxygen, as in spacecraft orbital environments, formation of FeF_3 and subsequent catalytic PFPE decomposition is potentially a significant degradation pathway for PFPE under boundary lubrication conditions.

3. The formation of FeF_3 through the denalogenation of PFPE by iron requires temperatures in excess of 500°C. Thus, 500°C represents a minimum estimate of temperatures that can be present in asperity contact regions.

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